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N-doped hierarchical porous carbon anchored tiny Pd NPs: A mild and efficient quinolines selective hydrogenation catalyst

Fengwei Zhang[a,1,*], Chunlan Ma[a,b,1], Shuai Chen[c], Jianfei Zhang[a], Zhihong Li[a], Xian-Ming Zhang[a,*]

[a] Institute of Crystalline Materials, Shanxi University, Taiyuan 030006, PR China
[b] Institute of Molecular Science, Shanxi University, Taiyuan 030006, PR China
[c] Analytical Instrumentation Center, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China

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ABSTRACT

Chemoselective hydrogenation of quinolines is often subjected to the problems of leaching and poisoning of catalytic active site as well as harsh reaction conditions. Developing a novel and high-performance heterogeneous catalyst is of paramount importance yet a huge challenge. Herein, we report a facile and efficient strategy for preparing the large surface area and highly N-doped hierarchical porous carbon anchored tiny Pd NPs catalyst, in which the low-cost chitosan, nitrogen-rich ionic liquids are served as composite precursors and KZ molten salt as friendly pore-forming agent. And a series of Pd@CIL-T (C refers to chitosan, IL refers to ionic liquid, T = 600–900 °C) catalysts are successfully fabricated via pyrolyzing aforesaid composites at different temperatures followed by anchoring the highly dispersed and small-sized Pd NPs on their surface. Among all the prepared catalysts, Pd@CIL-900 exhibits the optimal catalytic performance towards the selective hydrogenation of quinoline under extremely mild conditions (0.6 mol% Pd, 0.1 MPa H_2 and 50 °C). The kinetic experiments further reveal that such hydrogenation is subject to a pseudo-first order reaction and the apparent activation energy is as low as 41.1 kJ/mol, demonstrating excellent hydrogenation reaction rate. Moreover, the catalytic activity and selectivity are well maintained even after being reused for fifth reaction cycles.

1. Introduction

The chemoselective hydrogenation of quinoline and its derivatives is a fascinating transformation because the hydrogenated products 1,2,3,4-tetrahydroquinolines (py-THQs) play crucial roles in the production of fine chemicals, agrochemicals, pharmaceuticals and other bioactive molecules [1–5]. The hydrogenation of quinoline compounds generally involves multiple intermediates and high reaction energy barriers, which makes the reaction process inherently kinetically sluggish and thus presents great challenges to the development of high-performance catalysts [6–8]. It is acknowledged that the Ru, Rh, Au, Pt and Pd-based heterogeneous catalysts have been successfully applied to the selective hydrogenation of quinoline compounds [9–12]. Regrettably, existing catalysts are always hampered by problems of large amount of catalysts, harsh reaction conditions and relatively sluggish reaction rate [13,14]. Thus, searching for a suitable and efficient heterogeneous catalyst that can operates the highly selective hydrogenation of quinoline compounds under mild condition is of great significance in industrial applications.

Very recently, the carbon-based catalytic materials, which possess unique chemical, electronic and structural features, have been widely studied and considered as promising candidates to substitute commercially available noble-metal supported catalysts in the fine chemical synthesis and practical fuel cell applications [15–18]. Driven by these potential advantages, an innovative and multifunctional catalytic material based on heteroatom-doped carbon (phosphorus, boron, sulfur and nitrogen) has become a land for the development of highly efficient and stable integrated catalyst [19–24]. Among various kinds of heteroatom-doped carbon materials, the N-doped carbon is of particular interest owing to its excellent chemical stability, electrical conductivity as well as strong coordination interaction with metal nanoparticles [25–27]. N-doped porous carbon materials are typically synthesized through high-temperature pyrolysis of macrocyclic complexes [28], ionic liquids [29,30], nucleobases [31], deep-eutectic solvents [32] and polycarbon nitride [33] in the presence of hard templates or direct pyrolysis of metal-organic framwork precursors followed by additional

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* Corresponding authors.
E-mail addresses: fwzhang@sxu.edu.cn (F. Zhang), xmzhang@sxu.edu.cn (X.-M. Zhang).
[1] Chunlan Ma, which contributed equally as the first author.

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activation treatment [34]. However, the high cost, low natural abundance of feedstocks, skeleton collapse and unfriendly post-processing strategy are significant obstacles to their wider application. Therefore, a novel synthetic approach is urgently needed to prepare N-doped porous carbon with high specific surface area and rich pore structures, thereby overcoming current problems of nanoparticle aggregation/leaching under relatively harsh reaction conditions.

In continuation of our interest in nanoporous carbon-based catalytic materials [35], herein, we report the successful preparation of a novel hierarchically porous N-doped carbon materials using chitosan, ionic liquids and KZ molten salt [36,37] as carbon, nitrogen and pore-forming agent, respectively. Due to its large surface area, rich pore structure and high dispersity of Pd NPs, our home-made N-doped hierarchical porous carbon anchored tiny Pd NPs display superior catalytic activity and selectivity under extremely mild conditions (0.6 mol % Pd, 0.1 MPa H_2 and 50 °C) toward quinoline compounds hydrogenation compared with commercial 5 wt% Pd/C catalyst. The superiority of such catalytic system is as follows: i) the formation of large specific surface area and hierarchical porous support can increase the contact area and make reactants more accessible to the active sites; ii) the well-dispersibility of Pd NPs can increases the number of active sites and improve the catalytic activity; iii) the different types of nitrogen species (pyridinic-, pyrrolic- and graphitic-N) can enhance the adsorption capacity of quinoline compounds through hydrogen-bonding and π-π stacking interactions. Additionally, the synthetic methodology involved in the present work is expected to provide new avenues for developing other efficient catalysts in a simple and feasible way.

2. Experimental

2.1. Chemical reagents

1-bromobutane (98%), 3-picoline (99%), $PdCl_2$ (99%), $NaBH_4$ (98%), quinoline and its derivatives were provided by Aladdin Chemical Reagent Co., Ltd. $NaN(CN)_2$ (96%) was purchased from Meryer Chemical Technology Co., Ltd. Chitosan, $AgNO_3$, KCl and $ZnCl_2$ were purchased from Sinopharm Chemical Reagent Co., Ltd. All of other chemicals are used as received without any further purification. Deionized water was used throughout the experiment.

2.2. Synthesis of 1-butyl-3-methylpyridine dicyanamide ionic liquids (BMP-dca ILs)

17.0 g of $AgNO_3$ was dissolved in 100 mL of deionized water, and then 8.9 g of $NaN(CN)_2$ was slowly added into the $AgNO_3$ aqueous solution under stirring. After 2 h reaction, the genarated suspension was filtered and washed with an excess amount of deionized water, and the $AgN(CN)_2$ white solid was obtained. 46.6 g of 3-picoline was added into a 250 mL three-neck flask, and then 68.5 g of 1-bromobutane in a constant pressure funnel was dropped into the flask within 2 h with assistance of violent agitation. The mixture was then continuously stirred 15 h at 100 °C, and the dark red viscous liquid was produced when it was cooled to room temperature. To obtain high purity of 1-butyl-3-methylpyridine bromide ionic liquids (BMP-Br ILs), the crude product was purified by dissolving the BMP-Br ILs into deionized water, and then washed three times with ethyl acetate to remove the possible 1-bromobutane or 3-picoline impurity. The BMP-Br ILs was then obtained after evaporation of the water under vacuum. Subsequently, 23.0 g of BMP-Br ILs was dissolved in 150 mL of deionized water, 17.8 g of $AgN(CN)_2$ white solid was then added into the above solution with magnetic stirring without light. After reaction 8 h, the light yellow AgBr solid was separated from the mixture and the filtrate was treated via vacuum-rotary evaporation to remove the water. Finally, the reddish brown BMP-dca ILs was obtained.

2.3. Synthesis of N-doped hierarchical porous carbon (CIL-T)

1.0 g of BMP-dca ILs, 2.0 g of chitosan, 9.0 g of KZ molten salt ($KCl:ZnCl_2 = 1:3.6$) and 15 g of steel balls (1–2 cm in diameter) were ball milled at 800 r/min speed for 1.0 h. The generated homogeneous mixture was placed into a quartz porcelain boat and pyrolyzed at 600 ~ 900 °C (heating rate: 5 °C/min) for 2 h under flowing N_2 gas and cooled naturally to room temperature. Then, the black solid was thoroughly washed with deionized water to remove the KZ molten salt, and the obtained sample is denoted as CIL-T (C refers to the chitosan, IL refers to the ionic liquid, T represents the carbonization temperature). It should be noted that the KZ molten salt can be used for the next cycle after removing the water via vacuum distillation. As comparison, the identical procedure was applied to prepare C-900, IL-900 and CIL-900-w/o KZ based N-doped carbon materials except using BMP-dca ILs, chitosan as starting materials or without the addition of KZ molten salt.

2.4. Anchoring the Pd NPs on N-doped hierarchical porous carbon (Pd@CIL-T)

The Pd@CIL-T catalyst was prepared through a simple wet impregnation method. Take Pd@CIL-900 as an example, 1.0 g of CIL-900 support was dispersed in 100 mL of ethanol under ultrasonic oscillation at room temperature, and then 50 mL of 5.6 mM $PdCl_2$ aqueous solution was slowly added into the suspension dropwise under vigorous stirring. After being absorbed and coordinated for 12 h, 50 mL of 30 mM $NaBH_4$ was added into the above mixture, and the mixture was continued to stir for 4 h. The obtained black powders was filterd and washed several times with deionized water and ethanol, and dried in vacuum at 50 °C overnight for catalytic test.

2.5. General procedure for the selective hydrogenation of quinoline compounds

Typically, 1.0 mmol of quinoline compounds, 6 mL of solvent and a certain amount of Pd@CIL-T catalyst were added into a 50 mL PTFE reaction vessel or thick walled pressure vessel. The mixture was stirred for 2 min to ensure complete dispersion of the catalyst and then placed in a 50 mL stainless-steel autoclave. After being flushed three times with H_2, the pressure was elevated to 1–10 atm at room temperature. The autoclave was then heated to 30–120 °C with a magnetic stir for a certain time. Subsequently, the catalyst was removed from the mixture by centrifugation, and the liquid sample was analyzed by GC or GC–MS. The calculations of conversion and selectivity were based on the following formula: Conversion = [consumed substrate]/[initial substrate] × 100%, Selectivity = [py-THQs]/[all hydrogenated products] × 100%.

2.6. Characterization

Transmission electron microscope (TEM) was carried out on a FEI Tecnai G2 F20S-Twin using an accelerating voltage of 200 kV. For sample preparation, the powders were dispersed in ethanol with the assistance of sonication, and then one drop of suspention was slowly dropped onto a micro grid and dried with Infrared lamp irradiation. The distribution state of various elements in the Pd@CIL-900 catalyst was corroborated by scanning transmission electron microscopy coupled energy-dispersive X-ray spectroscopy (STEM-EDS) element mapping. XRD measurements were conducted on Rigaku Ultima IV diffractometer using Cu-Kα radiation as the X-ray source in the 2θ range of 10–80°. Fourier transform infrared (FTIR) spectra were obtained using a Thermo Nicolet iS5 spectrophotometer (frequency range from 4000 to 500 cm^{-1}) with KBr pellets. The metal dispersion was carried out using a Builder PCA-1200 chemical adsorption instrument. Prior to testing, Pd@CIL-900 catalyst was pretreated in argon at 150 °C for 60 min. The N_2 adsorption-desorption isotherms were obtained on an